Purification of La by Extraction Chromatography (抽出クロマトグラフィーによるランタンの高純度化)

著者	李 光燮
号	53
学位授与番号	4153
URL	http://hdl.handle.net/10097/42567

	リ　クァン　ソプ
氏　　名	李　光　燮
授　与　学　位	博士（工学）
学位授与年月日	平成２１年３月２５日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）知能デバイス材料学専攻
学位論文題目	Purification of La by Extraction Chromatography （抽出クロマトグラフィーによるランタンの高純度化）
指　導　教　員	東北大学教授　一色　実
論文審査委員	主査　東北大学教授　一色　実　　東北大学教授　佐藤　譲 東北大学教授　鈴木　茂

論文内容要旨

High purity La_2O_3 is required for application of target material. The main purpose of the research is to prepare the high purity La_2O_3. To obtain the high purity La_2O_3, extraction chromatography using D2EHPA impregnated resin is used as the main purification method to obtain the high purity La_2O_3. Also, a strong base polystyrene-divinylbenzene quaternary amine type of anion exchange resin (DIAION SA 10A) was applied for the separation of the impurities which cannot be removed by extraction chromatography using D2EHPA impregnated resin. Experiments were carried out at room temperature and in HCl media. Prepared La_2O_3 from purified $LaCl_3$ solution by calcinating La oxalate precipitated is evaluated by GDMS. The contents are summarized as follows.

Chapter 1 described needs of high purity La_2O_3 as high-κ dielectric material and the purification method of rare earth elements such as ion exchange, solvent extraction, and extraction chromatography. Also, a practical research objective and originality are defined from the issues pointed out.

Chapter 2 examines the relationship between extraction chromatography and solvent extraction via batch experiment. Also, performance of solvent impregnated resin using D2EHPA, PC88A, Cyanex 923 as solvents is investigated by batch experiment as functions of ratios between resin and metal solution and HCl concentration to find the optimum solvent impregnated resin. As a result, Cyanex 923, PC88A impregnated resin is not suitable for the separation of Ce, Pr, Nd, and Sm from La, because of the low adsorption ability for the tested elements. However, D2EHPA impregnated resin has the high adsorption ability and the large separation factors of the examined elements over La. Therefore, D2EHPA impregnated resin is found to be the most appropriate resin among the tested solvent impregnated resins.

In addition, relation between the logarithms of the distribution coefficients of the examined elements on D2EHPA impregnated resin and the equilibrated pH was estimated and represented by a straight line of slope three. This indicates that the mechanisms of solvent extraction and sorption by solvent impregnated resin are identical.

In chapter 3, from the results of chapter 2, D2EHPA impregnated resin was used for separation of impurities from La. The batch experiments were carried out in order to obtain the distribution coefficients of La and its major impurities on D2EHPA impregnated resin and the separation factors were also estimated from the results of the distribution coefficients. As a result, the separation factors of the divalent or trivalent elements were smaller or larger than unity, respectively. In addition, adsorption behaviors of the examined elements on D2EHPA impregnated resin were well explained by the extraction mechanism of solvent extraction using D2EHPA.

Based on the results of the distribution coefficients and the separation factors, the extraction chromatography for La purification was carried out using D2EHPA impregnated resin as stationary phase. The flow rate and the height of the resin bed were varied in this experiment. It is found that the slower flow rate and the higher bed height were desirable. The slowest flow rate and the highest bed height tested in this work were 1 $ml \cdot min^{-1}$ and 180 mm, respectively, for the resin bed with 25 mm diameter, and it was confirmed that this condition was suitable for practical use in the low La concentration.

Moreover, based on the optimum condition in the low La condition, the separation of impurities from La is carried out by extraction chromatography using the D2EHPA impregnated resin and anion exchange by DIAION SA-10 in the high La concentration and HCl media. Although there is a problem of decreasing equilibrated pH, height of bed resin and volume of loading solution is controlled to solve the problem. Also, column experiment is carried out by changing of La concentration to find a best condition for separation of impurities from La. The optimum condition of 360 mm height of resin bed and high La concentration is obtained. Furthermore, the column experiment of semi-pilot column with diameter 50 mm and 720 mm height of resin bed is carried out in La 15 $g \cdot dm^{-3}$. However, there is a problem of the Bi removal from La, because Bi has the same elution curve with La.

Anion exchange resin of SA-10 is used for removal of Bi. The condition of Bi removal is 1 $mol \cdot dm^{-3}$ HCl La chloride solution, 1 $ml \cdot min^{-1}$ flow rate in the small column. Consequently, it was confirmed that the separation of La and other impurities was possible by a method of extraction chromatography using D2EHPA impregnated resin and anion exchange using SA-10.

Chapter 4 describes the preparation of high purity La_2O_3 from purified $LaCl_3$ solution prepared in chapter 3 by oxalate precipitation method. Also, purity of the specimens and the overall process efficiencies are compared and interpreted. Furthermore, purity of prepared La_2O_3 is evaluated by glow discharge mass spectrometry (GDMS). According to the oxalate precipitation method, the optimum condition of La_2O_3 preparation is obtained as 50 ml of oxalate solution (0.65 mol), and heating at 1083 K for 2 h under O_2 atmosphere. Metallic impurities from prepared La_2O_3 were evaluated by GDMS. Table 1

displays the impurity concentration detected by GDMS. The first (A) sample shows the data of La_2O_3 obtained directly by oxalate precipitation of the starting material ($LaCl_3$ solution without treatment of D2EHPA impregnated resin and anion exchange separation). The second (B) sample shows the data of the La_2O_3 obtained by oxalate precipitation from $LaCl_3$ solution purified only by the D2EHPA impregnated resin. The third (C) sample shows the data of the La_2O_3 obtained by oxalate precipitation from $LaCl_3$ solution purified by anion exchange and then D2EHPA impregnated resin. The froth (D) sample gives the data of commercial 5N La_2O_3.

Table 1 The GDMS analysis of La_2O_3.

Elements	(A)	(B)	(C)	(D)
Rare earth elements / mass ppm				
Sc	0.012	<0.01	<0.01	<0.01
Y	0.640	<0.01	<0.01	0.110
Ce	8.40	0.370	0.490	0.100
Pr	3.70	1.56	0.340	4.17
Nd	3.70	0.085	0.096	1.52
Sm	5.70	0.120	<0.01	0.370
Eu	3.20	0.440	0.039	1.42
Gd	3.10	0.087	<0.01	0.400
Dy	0.022	0.018	<0.01	0.850
Yb	0.850	0.016	<0.01	0.270
La_2O_3/TREO (%)	99.9953	99.9996	99.9998	99.9989
Non-rare earth elements / mass ppm				
Mg	1.53	1.89	1.43	1.69
Al	10.26	7.27	2.61	4.68
K	6.23	4.55	4.40	6.21
Ca	9.52	2.23	1.77	5.73
Cr	3.18	2.86	0.400	1.04
Mn	2.56	2.06	0.049	1.31
Fe	3.11	2.74	3.42	4.65
Cu	0.450	3.43	0.220	2.88
Zn	0.510	0.580	0.110	2.76
Ga	1.13	0.200	0.063	0.054
Se	0.790	2.11	0.160	4.26
Sn	4.03	0.290	0.510	3.31
Hf	0.020	0.390	0.010	<0.01
Ta	9.51	1.76	0.900	10.61
W	0.010	0.360	<0.01	0.026
Pt	0.450	0.350	<0.01	0.440
Bi	0.400	0.340	<0.01	<0.01
Purity (%)	99.967	99.994	99.996	99.992

A: La_2O_3 prepared by raw material $LaCl_3 \cdot 7H_2O$ (99.1%), B: La_2O_3 prepared by treatment extraction chromatography

C: La_2O_3 prepared by treatment of anion exchange and extraction chromatography, D: Commercial 5N La_2O_3

The purity of produced La_2O_3 increased from 99.967% (A) to 99.994% (B) according to the D2EHPA impregnated resin separation. Also, it is confirmed that the purity of La_2O_3/TREO (Total Rare Earth Oxide) remarkably increased from 99.9953 (A) to 99.9996 (B) as the D2EHPA impregnated resin separation is adopted. All rare earth elements could be reduced to less than 1 mass ppm except Pr (1.56 mass ppm), so that the D2EHPA impregnated resin separation is very effective for elimination

of rare earth elements from La. In case of the (C) sample, purity of La_2O_3 is 99.996% and La_2O_3/TREO becomes 99.9998% by both the anion exchange and D2EHPA impregnated resin separation. It is confirmed that all rare earth elements could be reduced to less than 1 mass ppm. The impurities of some transition elements such as Al, Cr, Mn, and Cu also reduced in this process. In addition, the total purity including rare earth elements and non-rare earth elements is better than that of commercial 5N La_2O_3. It can be concluded that D2EHPA impregnated resin is effective for the separation of rare earth elements from La and anion exchange resin is useful for the separation of some transition metals. Flow sheet of "Preparation process of high purity La_2O_3" is summarized in Fig. 1.

Finally it can be concluded that extraction chromatography using D2EHPA impregnated resin is excellent method to separate rare earth elements from La and anion exchange resin is useful for the separation of some transition metals. Also, this method is a very simple process compared to the other purification methods. Accordingly, it is confirmed that the purification process developed in this research is suitable for preparation of high purity La_2O_3.

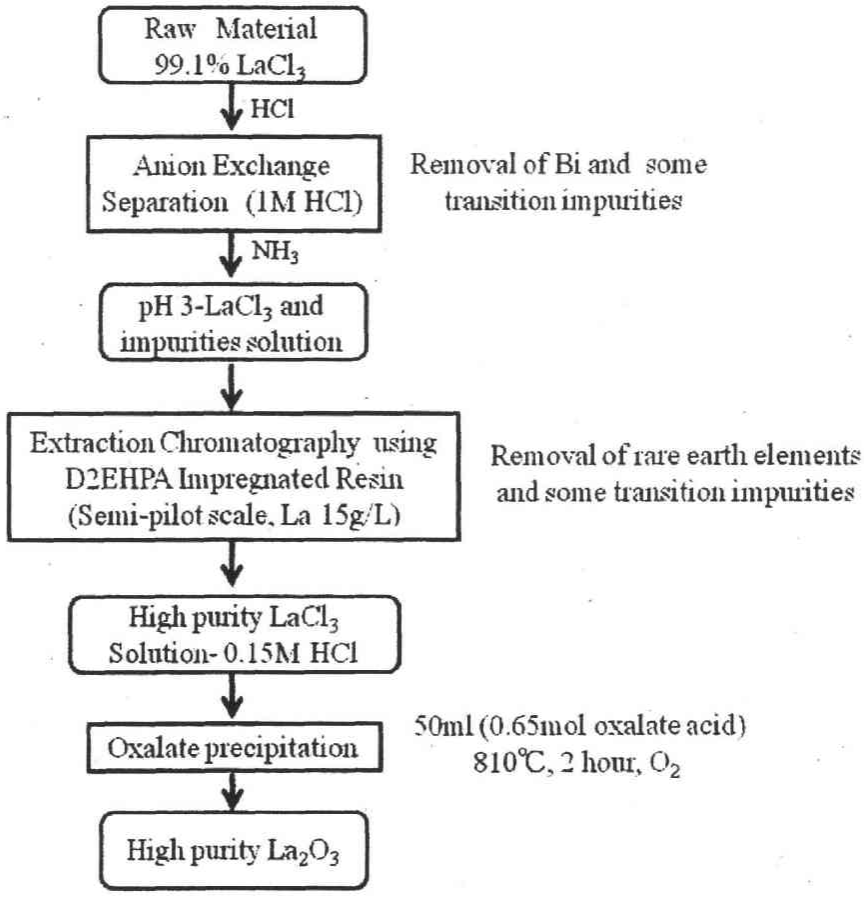

Figure 1 Preparation process of high purity La_2O_3.

論文審査結果の要旨

希土類金属は、その特性の多様性からさまざまな分野への応用がなされている。特に、La_2O_3は次世代ULSI のゲート絶縁膜材料として期待されている。ULSI に代表される電子デバイスに使用される材料は高純度である事が要求されるが、希土類金属元素は化学的に活性で、相互分離が困難であるために高純度化が遅れている。さらに、希土類金属の特性解明および新たな応用範囲の開拓のためにも高純度希土類金属の作製が不可欠である。本研究は、有機抽出剤含浸樹脂を固定相に用いた抽出クロマトグラフィーによる高純度La_2O_3の作製プロセスを開発したもので、全５章より成る。

第１章は緒論であり、本研究の背景と目的について述べている。

第２章では、有機抽出剤含浸樹脂を作製し、塩酸酸性水溶液中における La、Ce、Pr、Nd および Sm の分配係数を評価し、希土類金属元素の相互分離の可能性を調べている。抽出挙動の異なる３種類の有機抽出剤、Cyanex923、D2EHPA および PC88A に注目し、これらを市販のポーラス樹脂中に含浸させ、固定相と水溶液相の体積比および pH を変化させて分配係数の評価を行った。その結果、D2EHPA 含浸樹脂が La からの希土類金属不純物の分離に適していることを明らかにしている。

第３章では、D2EHPA 含浸樹脂を用い、希土類金属に多く含まれる非希土類金属不純物の分配係数および分離定数を評価し、抽出挙動の考察と、カラム法による分離条件を明らかにしている。抽出挙動は溶媒抽出の場合と同等であること、カラム法による分離が可能であることを明らかにした。特に、カラム法による分離では、実操業を目的とした、La の高濃度水溶液を用いた場合に生じる pH 変化の問題を解決している。

第４章では、カラムのスケールアップを行い、高純度 La_2O_3 を作製し、その純度を評価している。スケールアップ時に生じる問題を克服すると共に、抽出クロマトグラフィーでは除去が困難な Bi 分離に対して陰イオン交換法を適用し、分離プロセスを構築した。さらに、高純度化された La 塩化物水溶液からシュウ酸沈殿法により得られたシュウ酸塩を焼焼することで高純度 La_2O_3 を作製した。その結果、得られた高純度La_2O_3の純度は 99.996 %であり、希土類金属のみを考慮した場合の純度として、これまでの値を上回る 99.9998 %を達成している。

第５章は結論で、本研究で得られた成果を総括している。

以上要するに、本研究は、抽出クロマトグラフィーにより、これまで困難であった希土類金属の相互分離を目的とした基礎実験を行い、高純度 La_2O_3 を作製できるプロセスを開発したもので、材料工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。